RECOVERY OF WAX
AND
BY-PRODUCTS FROM BAGASSE

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ARMOUR INSTITUTE OF TECHNOLOGY

1913

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The recovery of wax and
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THE RECOVERY OF WAX AND OTHER BY-PRODUCTS FROM BAGASSE

A THESIS

PRESENTED BY

EARLE WATSON McMULLEN

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF CHEMICAL ENGINEER

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THE RECOVERY OF WAX AND OTHER BY-PRODUCTS FROM BAGASSE.

1. Historical:-

Since the first sugar-cane was crushed in crude mills to extract the juice, the bagasse or refuse fiber has been burned as fuel. There have been attempts in the past to utilize this evident waste in a more scientific and economical manner, but almost without exception, these have been a failure until the last four years.

The reason for this is evident to any one who studies the industry carefully. The old method which is still used, consists in squeezing the juice from the cane. In the modern mills, the bagasse is washed with hot water to obtain more sugar, but the best practice leaves about twenty per cent or one-fifth of the original sugar. This sugar in the tropical countries in which the sugar-cane is raised, ferments very quickly in the moist

bagasse, with the result that in a few days, at most, the fiber becomes a putrid shiny mass, absolutely unfit for any commercial use. Hence at the present time, the fiber is burned as quickly as possible after the sugar is extracted from it.

About four years ago, a new process, called the McMullen process was tried out in the tropics and this country. This process was the result of an endeavor to utilize the bagasse in a better manner, and to cut down the cost of manufacturing sugar. It consists of three distinct parts; first, the shredding and drying of sugar cane on the plantation; second, the importation of such dried, baled cane into the country where the sugar is to be marketed, where the sugar is washed out with water, refined and sold; third, the utilization of the sugar free fiber. It is on this latter subject that this present work was undertaken.

The first thought that comes to mind in the utilization of a woody fiber is - can it be used for paper? This has been tried with bagasse as ordinarily

obtained, for some years with more or less discouraging results. The reasons were many but may be summed up as follows; first, the sugar laden bagasse could not be shipped without being dried which was commercial failure; second, paper-making in the tropics is almost uniformly impossible due to the lack of pure water; third, the expense of removing the last trace of sugar was excessive; and fifth, the processes for the manufacture of paper from this stock were faulty.

However, with the sugar-free fiber obtained in a paper-making country by this new process as described, the manufacture of paper from it has proven a complete success and is now being carried on in a fairly large commercial plant.

As is commonly known in the paper industry, the yield of actual paper fiber from any woody stock is from forty to sixty per cent with the former as the more common figure. With the sugar-cane

fiber as above described, the yield has been pushed up to sixty per cent and even above by the most careful handling and scientific manipulation. However in this age of complete utilization of products, the remaining forty per cent became of interest.

It has been known for many years that the outside rind of sugar-cane was covered with a very thin film of wax. Some investigators by carefully scraping the outside film from many canes, obtained twenty-five to fifty grams of an impure wax which they purified by recrystallization from hot alcohol. Browne reports the pure wax as chiefly myricyl alcohol with a formula $C_{24}H_{50}O$. This is a normal saturated alcohol, melts at 82° C., boils at 146°C., is decomposed on continued heating into a hydrocarbon $C_{24}H_{48}$ and water. This latter property became of interest later in this work. Myricyl alcohol is soluble in hot organic solvents such as alcohol, ether,

chloroform, and benzine, but is almost insoluble when the solvent is cold and is insoluble in water.

Wijnberg reports that the wax is almost absent in some varieties of cane, but is present in others as high as .6 of one per cent. He obtained samples of wax by allowing the press cake or filtered material from the purification of cane juice to lie in heaps on the ground and ferment. The wax remained unchanged. The "mud" was dried and extracted with ether, or benzine. The product was then recrystallized from solution, re-dissolved, bleached with fuller's earth and re-crystallized from solution. He obtained a firm hard wax melting from 82 to 88° C. which he analyzed as follows:-

Analysis of cane wax Wijnberg	Glycerides of oleic, linolic palmitic and stearic acids, with hydroxyacids, resinacids, lecithin phytosterol and color	70. %
	Myricyl alcohol	13.5%
	Unnamed alcohol ($C_{33}H_{68}O$)	16.5%

It may be seen that this is a very impure body as might be expected from such a process. He simply ob-

tained all the bodies in the press cake soluble in hot benzine. It proves, however, the possibilities of this wax as his product is on the market and brings a fair price impure as it is. The above processes however are not very profitable as the wax is the only product obtained and the processes are expensive.

WORK PERFORMED.

Before starting any work on the recovery of wax from cane fiber, the analysis of the fiber was studied carefully for any hints which might be obtained. The following were the best available for the three parts of the cane:-

ANALYSIS OF CANE FIBER.

	Pith	Fibers	Rind
Cellulose (C&B)	49.00	50.00	51.09
Ash	1.68	3.58	1.64
Fat and Wax	.41	.72	.98
Protein (total nitrogenous bodies)	1.94	2.00	2.19
Pentosans (Furfuroids)	32.04	28.67	26.93
Lignin	14.93	15.03	17.17

The nitrogenous bodies are divided as follows, using the percentages on the raw cane not on the fiber alone.

	% in Raw Cane.
Albumen (coagulable & soluble in pepsin)	.059
Nuclein (coagulable & insoluble in pepsin)	.040
Albumoses and Peptones (not coagulable)	.033
Amide acids (Aspartic acid)	.145
Amide acids (Asparagine)	.232
Ammonia	.008
Nitrate	.071
Total % in cane =	.588

These nitrogen compounds received uninteresting at first, but later proved a valuable asset.

It was first thought possible to extract the wax from the whole dried cane before the sugar had been extracted. This was attempted using warm methyl alcohol as a solvent. The attempt was without great success although some wax was obtained mixed with many impurities which were separated with great difficulty. This method was impractical since the waste in solvent was of more value than the entire wax content of the cane.

In the same way, the extraction of the fiber with the sugar removed, proved a failure, both as to the quantity and purity of the wax obtained and the enormous loss of solvent. In this connection it is interesting to note, that in all these trials it took from ten to twenty times the weight of the fiber as solvent to extract the wax and other compounds and at no time was the loss in solvent less than the weight of the fiber.

After the failure of these methods, it was assumed that when the fiber was cooked with a solution containing essentially NaOH, to produce a paper pulp, that the cooking liquor would contain the wax or at least part of it. It became necessary to devise a means whereby the wax, if any were present, could be extracted from such a strongly alkaline liquor. After a great many unsuccessful attempts the following method was found to be the best. The author believes that this can be improved greatly but it will require very extended time and larger apparatus than was at hand.

The waste lye liquor from the paper cook must be boiled down to considerable thickness in order to obtain a concentrated solution which makes the separations possible. It is then neutralized or partially neutralized with acid - ether - hydrochloric or sulphuric, depending on whether the sodium chloride or sodium sulphate is wished as a final ignition product. The exact point to which the addition of acid is carried is difficult to determine, but should be such that the wax, an alcohol, is freed from the alkali according to the following reaction

$$C_{24}H_{47}ONa + HCl = C_{24}H_{47}OH + NaCl$$

The theory is that the strong alkaline cook forms a sodium myricylate which reforms the alcohol on addition of acid. It is also desireable at this point to prevent the excessive separation of resin acids as they settle to the bottom and prevent efficiency in boiling.

The amount of separated wax is so small in comparison to the bulk of the entire solution, that it will not form a cake on the surface and must be assisted by some cake-forming substance. While many substances are available for this purpose, it has been found by many trials that pure castile or other soap gives the best results as it is insoluble in the presence of much inorganic salt. In ordinary caustic liquor, the amount of salt produced by the neutralization of the alkali with acid is not sufficient to completely precipitate the soap; therefore to such a liquor a small quantity or common salt must be added or another cake forming substance such as paraffine, stearic acid, beeswax etc. must be used. As any of these latter are a little more difficult to separate from the wax, the former method is advised, although further study of the properties of the wax may lead to new and improved methods of separation.

In a new cooking liquor devised for the paper manufacture from bagasse, a large quantity of salt is

present and hence obviates the difficulty mentioned.

This cake is separated from the liquor by any suitable method. In the laboratory it was skimmed off, while in a plant, the liquor could more readily be drawn off from the top layer. The cake is dissolved in any suitable solvent - boiling alcohol has proven the best so far as both substances, the wax and soap, are soluble therein. On cooling, the wax partially precipitates and does so completely on diluting the solution with water. The soap remains completely soluble in the water and alcohol mixture and hence the wax may be filtered off without much difficulty.

Another method of separation is to dry the cake and extract with hot benzine, chloroform or ether. This has given fair results and the only way to determine the choice of the best method is the cost in a commercial plant.

The impure wax filtered from the soap solution or obtained by distilling off the benzine or other sol-

vent, may be purified by re-dissolving in hot alcohol, re-crystallizing out by cooling and obtained in a very pure state.

The soap solution may be distilled to recover the alcohol and leave the soap solution in water to use over again. It is interesting to note that the loss of soap in the process is almost if not completely counterbalanced by the soap formed from the oils and fats in the cane fiber.

The liquor on further neutralization may act in several different ways, depending on the time and pressure of the cook and the composition of the cooking liquor.

In a small laboratory operation the gums and pectin or pectous substances were precipitated due to the neutralization with acid and the saturated brine solution. Pectin and allied substances are soluble in water but almost insoluble in saturated brine while liberated resins are insoluble in any

neutral or acid solution. This mixture of gum and pectin containing some salt, is readily filtered off. These products may be separated in several different ways but two seem better than the others:

The cake is broken up, as it is solid on cooling and extracted with warm but not boiling water. This extracts the pectin and salt and leaves the gum or resin acids in a fairly pure state.

The pectin is somewhat difficult to separate from the salt but the following method is fairly efficient. A small quantity of milk of lime or preferably barium hydroxide is added to the pectin salt mixture, the pectin forms a salt with barium or calcium which is fairly insoluble in cold water. The solution is cooled and the barium or calcium pectate filtered off. The pectin may be recovered by careful neutralization with dilute sulphuric acid or by carbonation with

carbonic acid gas. Either method will form a precipitate of barium or calcium sulphate or carbonate from which the pectin solution is filtered. The pectin may be recovered by evaporating the water or by the addition of sufficient alcohol to precipitate it.

In some liquors used in these experiments, particularly in the new liquor devised for use with the cane fiber, a considerable quantity of albumin coagulated on the first neutralization and settled to the bottom of the liquor. This could readily be removed as it was in solid masses and when warmed with dilute caustic dissolved to form an excellent size for paper. With some liquors, however, practically no albumin was formed, so that the production of this product depends almost entirely upon the liquor used.

The quantities of these products produced under the best conditions are very interesting from a commercial stand point. The best yield of wax yet obtained is about the equivalent of 100# per

ton of dry cane fiber. The average with other fiber does not seem to be so high but will approximate 50# per ton.

The amount of pectin is about 40 lbs. per ton of dry fiber while the gum runs from 80 to 85 lbs. The amount of albumin varied so much that it is difficult to estimate what could be produced commercially. From 30 to 35 lbs. would seem to be a fair figure.

The cost of production is very difficult to estimate due to the very small scale on which the operations were conducted. At the present time, the profit would be quite small due to the expensive operations required. It is believed, however, that these could be so cheapened as to yield a large margin of profit.

CONCLUSIONS.

While a great deal of work has been done on this most interesting problem, there is much more to be done. For instance, it has been found that on a prolonged cook with very strong alkali, no wax at all is found in the waste liquor. The author believes that this is due to the reaction of the wax before mentioned - namely, that on prolonged heating it decomposes into a hydrocarbon and water. It has also been found that a very light cook gives no wax. The paper from this light cook was found to contain the wax. Hence it becomes a question of whether it is desirable to extract the wax by a medium cook or to leave it in the paper. The author believes that this could be done at the discretion of the paper maker; that for brown papers where great strength and natural size were desired, the wax should be left in; for white papers of medium strength, the wax should be cooked away and recovered from the liquor.

There is at present no commercial source for large quantities of pectin. The author believes that such a commodity would be very valuable and desireable as it may be used for paper size, artificial jelly and for many other purposes. Its market value would be difficult to estimate until it had been tried out by the different industries for which it is suited.

The gum is a somewhat black product resembling low grade resin. Its great use or value is questionable although if large quantities were produced there is no doubt that a commercial use would be found.

The uses of albumin are too well known to discuss. Although the compound obtained by this process is somewhat impure, yet it would be valuable as paper size and many other uses where a pure product is unnecessary.

The uses of the wax are best described by comparing it to carnauba wax or the best bleached beeswax. It has a high melting point, is quite firm and hard and hence would take the place of the two waxes just mentioned.